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(54) Title: NEW TARGETABLE SOLIDS FOR POLYMER BLENDS AND METHODS OF MANUFACTURING THE SOLIDS AND BLENDS CONTAINING THE SAME

(57) Abstract

Solid, e.g., modified fillers and curatives, for polymers, elastomers, rubbers, polyolefins, and blends thereof, comprising a solid having the polymers, rubbers, polyolefins, and elastomers of the blend or polymers, rubbers, polyolefins, and elastomers compatible with the components of the blend coated or adsorbed thereon and methods of preparing the modified solids and blends containing the same.

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NEW TARGETABLE SOLIDS FOR POLYMER BLENDS AND METHODS OF MANUFACTURING THE SOLIDS AND BLENDS CONTAINING THE SAME

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to new, modified solids, e.g. fillers and curatives, for polymers, elastomers, polyolefins, rubbers, and blends thereof and methods of preparing the modified solids and blends containing the same. Generally, the invention relates to targetable solids for addition to polymer blends, i.e., solids which may be custom designed to locate themselves in specific polymer components of the blend.

Description of Related Art

Generally, solids have been utilized and/or incorporated into general purpose rubber (GPR), polymers, elastomers, polyolefins, and/or mixtures of the above. For example, in the tire industry, numerous solid fillers have been proposed for rubber and polymer blends in order to enhance the properties of tires, for example, to decrease the rolling resistance of tires by modifying the rubber compositions used for the treads of tires. Reinforcing white fillers such as silica, bentonite, clay, titanium oxide, talc, etc., have been proposed for use in tire treads which tend to decrease the resistance to travel of the tires having a tread comprising such fillers. Various fillers and processes for blending the same into rubber compositions have been proposed. For example, Rauline, in U.S. Patent No. 5,227,425, describes the use of a copolymer of a conjugated diene with an aromatic vinyl compound prepared in solution with a special silica, known *per se*, to obtain dispersion of the silica in the elastomeric matrix.

Raines, *et al.*, in U.S. Patent No. 5,017,630, describe an aqueous dispersion of silicone dioxide mixed with an emulsion latex polymer which is spray dried to achieve free-flowing, fine-sized particles of the polymer containing very high amounts of the silicone dioxide therein.

Morocskowski, in U.S. Patent No. 5,162,409, describes a rubber composition suitable for use in automobile tire treads wherein the composition comprises a halogenated isobutylene rubber which can be the sole rubber of the composition or one of a combination of rubbers. A preferred embodiment comprises a rubber component comprising 20 to 60 weight percent styrene/butadiene rubber, 20 to 60 weight percent butadiene rubber, and 10 to 30 weight percent of a halogenated rubber, a silica filler, and an organosilane cross-linking agent. It is disclosed that in a preferred embodiment, the rubber compositions comprise 10 to 30 parts per 100 parts rubber of untreated, precipitated silica employed with an effective amount of organosilane coupling agent, for example, 1 to 8 parts per hundred rubber.

Preferably, the filler reinforces all phases, i.e., the polymeric phase of a blend, and curing can be controlled for each polymer phase component of the blend. However, it is often discovered that the filler migrates from one polymer phase component to the other polymer phase component during processing. Consequently, these effects greatly limit the enhancement of properties that can be achieved with fillers, and the curing and cure state of articles made therefrom.

Generally, polymer blends, e.g., those used to produce tires, are often crosslinked. It is known that the physical properties, performance characteristics, and durability of vulcanized rubber compounds are directly related to the number (crosslink density) and type of crosslinks formed during the vulcanization reaction. (*See, e.g.*, The Post Vulcanization Stabilization for NR, W.F. Helt, B.H. To & W.W. Paris, *Rubber World*, August 1991, pp. 18-23 which is incorporated by reference herein.) Generally, polymer blends may be crosslinked by adding curative molecules, for example sulfur, zinc, metals, radical initiators, etc. followed by heating. This method may be accelerated and is often used for the vulcanization of elastomer blends. The mechanism for accelerated vulcanization of natural rubber involves complex interactions between the curative, accelerator, activators and polymers. Ideally, all of the available curative is consumed in the formation of effective crosslinks which join together two polymer chains and enhance the overall strength of the polymer matrix. Numerous curatives are known in the art and include, but are not limited to, the following: zinc oxide, stearic acid, tetramethylthiuram disulfide (TMTD), 4,4'-dithiodimorpholine (DTDM),

tetrabutylthiuram disulfide (TBTD), benzothiazyl disulfide (MBTS), hexamethylene-1,6-bisthiosulfate disodium salt dihydrate (ERP 390), 2-(morpholinothio) benzothiazole (MBS or MOR), blends of 90% MOR and 10% MBTS (MOR 90), N-oxydiethylene thiocarbamyl-N-oxydiethylene sulfonamide (OTOS) zinc 2-ethyl hexanoate (ZEH); and MC sulfur. In addition, various vulcanization systems are known in the art. (For example, see Formulation Design and Curing Characteristics of NBR Mixes for Seals, *Rubber World*, September 1993, pp. 25-30 which is incorporated by reference herein). A possible major problem with these methods of crosslinking is often the concentration of the curative molecules in some phase or phases of a blend is insufficient for good crosslinking due to migration or partitioning of the curative molecules between the phases of the blend during the mixing or blending process.

Therefore, there is a need for a method for the complete curing of polymer blends, elastomers, etc. wherein the concentration of curative in each polymer phase is predictable and controllable. There is also a need for a method for the preparation of mechanical blends of filled polymers, elastomers, etc. in which the concentration of filler in each polymer phase component is predictable and controllable.

SUMMARY OF THE INVENTION

According to one aspect, the invention is directed toward a method for the preparation of a targetable solid, i.e., a filler for addition to a rubber composition or a blend of at least two polymeric components. The method, according to one embodiment, comprises contacting or treating the filler with the polymer component of the blend having the least affinity for said filler as compared to the other polymer blend components, and thereafter contacting said first polymer treated filler with a second polymer component having a greater affinity for the filler. According to another embodiment, the filler contacted with the polymer components is further subjected to thermal curing under nitrogen atmosphere. It should be recognized that the invention is also directed to methods wherein the filler is contacted with a polymer or polymers which is/are not the same as either of the polymers of the blend but are compatible, i.e., generally miscible, with one or both of the polymers of the blend. The invention is also directed to a filler produced according to the above-described methods.

According to another aspect, the invention is directed toward a method for the preparation of a filled blend comprising polymer treated filler and polymer(s) blend components to produce a blend. The polymer blend comprises two or more polymer components with the treated filler dispersed throughout. The method comprises contacting or treating the filler with a minor amount of a polymer, which may, e.g., be the first component of the polymer blend. According to one embodiment of the invention, the first polymer has the least affinity for the filler as compared to other polymer for treatment of the filler. The filler, including said first polymer, is subsequently contacted with a minor amount of a second polymer having a greater affinity for said filler than said first polymer . Thereafter, the coated filler is mixed with the polymer(s) for forming the blend. The invention is also directed to a filled blend produced according to the above-described methods.

According to a further aspect, the invention is directed to a filler, e.g., a particle, for addition to a polymer comprising a first polymer and/or a blend of a first polymer with a second polymer. The filler has a coating thereon comprised of at least one polymer compatible with at least one of the blend polymer(s) or, e.g., at least one of the first or second polymer blend components.

According to a still further aspect, the invention is directed to a filled blend comprising a polymer blend comprising at least two polymers and a filler, said filler having at least one polymer compatible with at least one of the polymer blend components coated thereon.

The invention, according to another embodiment, is directed to methods for crosslinking polymer blends comprising at least two polymers. The method generally comprises pretreating the solid with a curative, mixing the pretreated solid with the two polymers of the blend to form a curable polymer mixture, and subjecting the blend to curing conditions, such as sufficiently heating the mixture to obtain crosslinking and/or curing.

The method of forming a solid comprising curative may, according to an embodiment, be accomplished by precipitation of a polymer from a solution comprising curative molecules, wherein the curative is the sole solid. According to a further embodiment, the method of forming a solid comprising curative comprises adsorption

of curative molecules onto an inert solid, isolation of the solid, and adsorption of a polymer onto the curative treated solid. According to a further embodiment, the method of forming a solid comprising curative may comprise adsorption of a polymer coating onto curative particles. According to a still further embodiment, the method of forming a solid comprising curative may comprise mixing curative with a solid to form a mixture, and adsorbing a polymer onto the mixture.

According to a still further embodiment, the present invention is also directed to polymer blends produced according to the above-described methods.

The present invention is further directed to curative precursors used in crosslinking polymer blends, said precursors produced from: (1) the precipitation of a polymer from a solution comprising dissolved or suspended curative molecules; (2) adsorbing curative molecules onto a solid, and adsorbing a polymer onto the solid; (3) adsorbing a polymer onto curative particles; or (4) mixing or grinding curative molecules together with an inert solid to form a mixture, and adsorbing a polymer onto the mixture. The invention is also directed to methods for making curative molecules.

DETAILED DESCRIPTION OF THE INVENTION

According to one embodiment, the present invention provides a composition based on a mixture or blend of rubbers, elastomers, polyolefins, polymers, etc. comprising a polymer blend or mixture and a solid. The solid may, for example, be a filler, such as silica, wherein the filler has coated thereon or has adsorbed on its surface one or more of the components of the polymer phase. According to another embodiment, the solid may be pretreated with a curative.

Rubbers, polymers (thermoplastic, thermoset and mixtures thereof), elastomers, and polyolefins and products produced therefrom useful in the practice of the invention include, but are not limited to, brominated butyl rubber (commonly called bromobutyl and as used herein, the term "butyl rubber" means a copolymer of isobutylene and a diene such as isoprene); chlorinated butyl rubber (commonly called chlorobutyl where isoprene is the diene copolymerized with isobutylene); star-branched polyisobutylene comprising branched or star-shaped polyisobutylene subunits, such as star-branched bromobutyl; isobutylene-bromomethylstyrene copolymers such as isobutylene\para-bromomethylstyrene, isobutylene/chloromethylstyrene copolymers such as

isobutylene/para-chloromethylstyrene, and the like halomethylated aromatic interpolymers disclosed in U.S. Patent No. 5,162,445 which is hereby incorporated by reference; isoprene and halogenated isobutylene copolymers (chlorinated or brominated); polychloroprene (neoprene); and the like, and mixtures thereof.

The invention is also preferably directed to blends comprising halogenated isobutylene rubbers including halogenated terpolymers comprising isobutylene such as halogenated isobutylene/styrene/dienes, for example, isobutylene/styrene/isoprene, and halogenated isobutylene/methylstyrene/dienes, for example, isobutylene/methylstyrene/isoprene; isobutylene/halomethylstyrene/diene terpolymers including isobutylene/bromomethylstyrene/isoprene; isobutylene/haloisobutylene/dienes, including isobutylene/bromobutylene/isoprene; and the like, and mixtures thereof with other halogenated isobutylene rubbers.

Other elastomers useful in the invention include: polybutadiene, BR; styrene-butadiene rubber, SBR; nitrile-butadiene rubber, NBR; natural rubber, NR; polyisoprene, IR; and ethylene-alphaolefin elastomers like ethylene-propylene rubber, EPR.

Thermoplastics useful in this invention include polyethylene, polypropylene, polystyrene, polycarbonate, and nylon.

Fillers which can be utilized in the practice of the present invention include, but are not limited to, silica, pumice, bentonite, clay, titanium oxide, talc, calcium carbonate, high styrene resins, coumarone-indene resin, phenolic resin, lignin, modified melamine resins, and petroleum resins. The fillers of the present invention may be any size and typically range, e.g., in the tire industry, from about 0.0001 to about 100 microns. As used herein, silica is meant to refer to any type or particle size silica or another silicic acid derivative, or silicic acid, processed by solution, pyrogenic or the like methods and having a surface area, including untreated, precipitated silica, crystalline silica, colloidal silica, aluminum or calcium silicates, fumed silica, and the like.

The curatives useful in the practice of the present invention generally include curatives used in the rubber industry, e.g., sulfur compounds, zinc compounds, metal compounds, radical initiators, etc. and include, but are not limited to, zinc oxide, stearic

acid, tetramethylthiuram disulfide (TMTD), 4,4'-dithiodimorpholine (DTDM), tetrabutylthiuram disulfide (TBTD), benzothiazyl disulfide (MBTS), hexamethylene-1,6-bisthiosulfate disodium salt dihydrate (ERP 390), 2-(morpholinothio) benzothiazole (MBS or MOR), blends comprising 90% MOR and 10% MBTS (MOR 90), N-oxydiethylene thiocarbamyl-N-oxydiethylene sulfonamide (OTOS) zinc 2-ethyl hexanoate (ZEH); and MC sulfur.

The compositions produced in accordance with the present invention may also contain other components and additives customarily used in rubber mixes, such as plasticizers, pigments, anti-oxidants, vulcanization accelerators, napthenic or aromatic extender oils if the presence of an extension oil is desired, and silane coupling agents, etc.

In a preferred embodiment, the polymer blend is comprised of a blend of two components, for example, polybutadiene and a brominated copolymer of isobutene and 4-methylstyrene or polymers compatible with polybutadiene and brominated copolymer of isobutene and 4-methylstyrene. Preferably, the filler utilized in the above-described preferred embodiment is silica having co-adsorbed thereon minor amounts of polybutadiene and brominated copolymer of isobutene and 4-methylstyrene.

In accordance with the practice of the present invention, a method is provided for the preparation of filler for addition to a blend of at least two polymer components selected from the group consisting of elastomers, rubbers, polyolefins, polymers and mixtures thereof. In accordance, a preferred embodiment of the invention before blending the filler with the polymer blend component(s), the filler is contacted with a minor amount of the polymer component which has the least affinity for the filler as compared to the other polymer components to form a stable surface saturated layer. The thickness of the layer may be varied by varying adsorption conditions. Depending upon the filler and the polymer(s), the adsorption time may range from about one second to several hours. It should be noted that depending upon the polymer, different solvents may be utilized including, but not limited to, aliphatic and aromatic solvents like pentane, hexane, and toluene. The adsorption may be conducted at low temperatures, e.g., -40° C where the amount of polymer to be adsorbed is large, to high temperatures, e.g., up to 200°0 C when the amount of polymer to be adsorbed is small.

For example, as further described below, when a polymer blend is comprised of a brominated copolymer of isobutene and 4-methylstyrene and polybutadiene, the filler, e.g., silica, is preferably first contacted with a minor amount of the brominated copolymer of isobutene and 4-methylstyrene. This copolymer has less affinity for said filler as compared to the polybutadiene. As used herein, the term "minor amount" means in an amount sufficient to provide a stable surface saturated layer on the filler. After contacting the filler with the brominated copolymer of isobutene and 4-methylstyrene, preferably forming a layer by the adsorption of the same onto the filler surface, the filler is contacted with a minor amount of the second component of the polymer blend and/or the polybutadiene. In this manner, a filler is provided which will not completely migrate from the brominated copolymer of isobutene and 4-methylstyrene during the blending of the two components of the polymer phase. Preferably, depending upon the application, after the filler has been contacted with the polymer blend components, the contacted filler is subjected to curing conditions such as to heat or thermal curing under a nitrogen atmosphere at temperatures ranging from about 60° C to about 120° C.

In order to determine which polymer has the least affinity for the filler as compared to the other polymer, it is useful to measure rates of competitive adsorption or co-adsorption of polymers, etc. onto solid particles. For example, to determine whether the brominated copolymer of isobutene and 4-methylstyrene has a greater or weaker affinity for the filler as compared to polybutadiene, the following test is performed which may be modified in accordance with that which is well-known in the art for other polymer phase component systems. Specifically, the exchange of elastomers on a silica filler was measured using a practical and rapid method comprising solid state H MAS-NMR. This method allows the possibility to monitor and rank polymer interactions with solid fillers by measuring the exchange.

The exchange was performed from both directions, that is, adsorbing from solution the brominated copolymer of isobutene and 4-methylstyrene (hereinafter "brominated copolymer") first and then placing the brominated copolymer-loaded silica filler into a solution of polybutadiene and *vice versa*. The polymer-loaded filler sample remained wet with solvent, e.g., one weight percent solution of pentane, during the

transfer to a solution, e.g., one weight percent solution, of the second polymer. After exposure to the solution of the second polymer for a time interval, a sample of the polymer-loaded filler was removed and washed in an excess of solvent. The composition of the resulting solvent was monitored by solid state H MAS-NMR which was used to measure the ratio of one polymer to another. This quantity can be measured precisely without any other standards. The total polymer composition was determined by carbon elemental analysis, and polymers in the same molecular weight were used.

The results of the exchange experiment in which the brominated copolymer was loaded first are shown in Table 1. To summarize, the polybutadiene rapidly replaced some, but not all of the brominated copolymer. The fact that some of the brominated copolymer was exchanged can be concluded by comparison of the elemental and H MAS-NMR analysis as follows: if all the carbon weight gain of Sample 3 represented adsorption of polybutadiene, then the Sample should be only [100 x (6.5-3.7) divided by 6.5] equals 43% polybutadiene. Since there was a much greater percentage of polybutadiene than 43% in Sample 3, polybutadiene had replaced some of the brominated copolymer. Most of the brominated copolymer, about 65% of the initial amount, was exchanged.

TABLE 1

Exchange of Brominated Copolymer-Loaded (EXXPRO®: brominated copolymer of isobutene and 4-methylstyrene)[1] HiSil 233 (silica) with Polybutadiene (Budene 1207)

Sample	Composition* by MAS-NMR	Time for Second Adsorption (Hr)	Weight % Carbon
1	100% E	0	3.7
2	67% B	0.25	6.7
3	76% B	24	6.5

[1] Brominated poly(isobutylene-co-4-methylstyrene) containing 7.5 wt% 4-methylstyrene and 2 wt% having a Mooney viscosity ML(1+8) 125° of 45±5

* E = EXXPRO® 90-10 (Brominated Copolymer of Isobutene and 4-methylstyrene) B = Budene 1207 (Polybutadiene)

The results of the exchange experiment in which polybutadiene is loaded first is shown in Table 2. No H MAS-NMR signals for the brominated copolymer were observed in the samples. Thus, no exchange of adsorbed polybutadiene by the brominated copolymer occurred.

TABLE 2

Exchange of Polybutadiene (Budene 1207)-Loaded Silica (HiSil 233) with Brominated Copolymer of Isobutene and 4-Methylstyrene (EXXPRO® 90-10)[1]

Sample	Composition* by MAS-NMR	Time for Second Adsorption (Hr)	Weight % Carbon
4	100% B	0	6.0
5	100% B	0.25	5.9
6	>94% B	24	5.8

[1] Brominated poly(isobutylene-co-4-methylstyrene) containing 7.5 wt% 4-methylstyrene and 2 wt% having a Mooney viscosity ML(1+8) 125° of 45±5

* B = Budene 1207 (polybutadiene)

As a result, it can be stated from the above that Budene 1207 (polybutadiene) tends to have a greater affinity or interaction with HiSil (silica) than does EXXPRO® 90-10 (brominated copolymer of isobutene and 4-methylstyrene).

Polymer blends exemplifying the present invention and analytical data supporting the same are set forth below. The examples illustrate that the modified or coated silica filler is well dispersed in a blend of brominated copolymer of isobutene and 4-methylstyrene and polybutadiene elastomers, whereas a conventional silica filler is not.

EXAMPLES I (Comparative) & II

Example I is the control in which EXXPRO® 90-10 (30 phr), Budene 1207 (70 phr) and conventional HiSil 233 (30 phr) are blended by milling together. The dispersion of the silica filler can be detected by scanning electron microscopy. The scanning electron microscopy showed that the conventional silica filler was not found to be present in the EXXPRO® phase of the blend. Coated silica used in this example was prepared by stirring for 30 minutes a suspension of 100 g. HiSil 233 in a 0.5 wt% polymer in cyclohexane solution. The coated filler was removed and washed with cyclohexane three times. On the other hand, when the modified silica filler of the present invention is used to make a similar blend, as in Example II, the modified silica filler of the present invention is found to be well dispersed in the EXXPRO® phase and the Budene phase.

Example II: Modified silica filler was prepared by adsorption of poly(isoprene) from dilute solution 0.5% polymer in cyclohexane, with vigorous stirring at about 22° C for approximately 1 hour. The coated silica was washed three times in cyclohexane. The weight percent carbon of the product was 6.18%. The above-described product was then subjected to heat or thermal curing under a nitrogen atmosphere at temperatures ranging from 60° C to 120° C for 60 minutes. The polyisoprene layer was extensively crosslinked because polyisoprene signals of the adsorbed polyisoprene layer were no longer observed in the solid state NMR spectrum. Crosslinked coatings formed in this example are stable to exchange by other polymers including polar polymers with a high affinity for the filler like NBR. These coated fillers will be primarily found in the polyisoprene regions when used in blends of polyisoprene and NBR.

The present invention also relates and generally applies, e.g., to various curing or vulcanization systems including, but not limited to, conventional systems (polysulfidic crosslinks produced by sulfur system); conventional systems with post vulcanization stabilizers, e.g., dihydrate of the sodium salt of hexamethylene-1, 6-bisthiosulfate-s-ester; EV systems (low concentration of sulfur and high concentration

of an organic accelerator); sulfurless or sulfur donor systems (using, for example, TMTD); Semi-EV (intermediate system between conventional and EV systems); Soluble EV and Soluble Semi-EV systems; and the EV System of Hofmann (combination of sulfur donors, like TMTD and DTDM, in conjunction with sulfenamide (OTOS).

The curative precursors of the present invention are generally comprised of a solid containing or comprising curative. The curative precursor of the present invention may be formed by, e.g., the following methods: (1) precipitation of a polymer from a solution containing dissolved or suspended curative(s); (2) adsorption of curative(s) onto an inert solid, e.g., alumina or silica, followed by isolation of the curative-loaded solid, and adsorption of a polymer coating to the surface of the loaded solid; (3) adsorption of a polymer coating to the surface of curative particles; or (4) mixing and/or grinding together curative(s) with an inert solid, followed by adsorption of a polymer coating to the surface of the resulting solid curative mixture. The polymers useful in the preparation of the curative precursors of the present invention may be comprised of the same polymers of the blend and/or polymers compatible with one or more polymers of the blend. The term "compatible" as used herein means generally considered miscible.

While the following discussion is in terms of a single embodiment, it is understood that the scope of the invention shall not be limited thereby. In accordance with the practice of the present invention, a method is provided for the preparation of curative precursors for addition to a blend of at least two polymers selected from the group consisting of, for example, but not limited to elastomers, rubbers, polyolefins, polymers and mixtures thereof. In accordance with the present invention, a curative loaded solid or solid curative is, according to one embodiment, contacted with one of the polymers of the blend and/or a polymer compatible with one or both of the polymers of the blend and the polymer is adsorbed onto the surface of the curative loaded solid or solid curative. According to a preferred embodiment, the solid curative precursor is contacted with a minor amount of the polymer of the blend which has the "least affinity" for the curative solid as compared to the other polymer(s) of the blend to form a stable surface saturated layer, e.g., which preferably is not removed by any

subsequent solvent extractions. The thickness of the layer may be varied by varying adsorption conditions. Depending upon the solid utilized to form the curative-loaded solid and the polymer(s), the adsorption time may range from about one second to several hours. It should be noted that depending upon the polymer, different solvents may be utilized including, but not limited to, aliphatic and aromatic solvents like pentane, hexane, and toluene. The adsorption may be conducted at low temperatures, e.g., -40° C where the amount of polymer to be adsorbed is large, to high temperatures, e.g., up to 200° C when the amount of polymer to be adsorbed is small. For example, as further described below, when the polymers are brominated copolymer of isobutene and 4-methylstyrene and polybutadiene, the curative loaded silica solid, is preferably first contacted with a minor amount of the brominated copolymer of isobutene and 4-methylstyrene. This copolymer has the "least affinity" for said loaded solid as compared to the polybutadiene. As used herein, the term "minor amount" means in an amount sufficient to provide a stable surface saturated layer on the filler. After contacting the curative-loaded solid with the brominated copolymer of isobutene and 4-methylstyrene, preferably forming a layer by the adsorption of the same onto the curative-loaded solid surface, the curative-loaded polymer coated solid is contacted with a minor amount of the second polymer of the blend and/or the polybutadiene. In this manner, a precursor is provided which will not completely migrate from the brominated copolymer of isobutene and 4-methylstyrene during the blending of the two polymers. Preferably, depending upon the application, after the curative loaded solid has been contacted with the polymers of the blend, the curative precursor is subjected to heat or thermal curing under a nitrogen atmosphere at temperatures ranging from about 60° C to about 120° C.

In order to determine which polymer of the polymer blend has the "least affinity" for the solid comprising curative as compared to the other polymer(s), it is useful to measure rates of competitive adsorption or co-adsorption of polymers, etc. onto solid particles. For example, to determine whether the brominated copolymer of isobutene and 4-methylstyrene has a greater or weaker affinity for the curative-loaded solid (which later forms the curative precursor) as compared to polybutadiene, the following test is performed which may be modified, if needed, for other polymer

systems. Specifically, the exchange of elastomers on a solid precursor may be measured using a practical and rapid method comprising solid state H MAS-NMR. This method allows the possibility to monitor and rank polymer interactions with solids by measuring the exchange.

According to one embodiment of the method of the invention, the curative-loaded, first polymer-coated solid of the precursor is kept wet with solvent, e.g., one weight percent solution of pentane, during transfer to a solution, e.g., one weight percent solution, of the second polymer. After exposure to the solution of the second polymer for a time interval, a sample of the polymer-coated precursor should be removed and washed in an excess of solvent. The composition of the resulting solvent may be monitored by solid state H MAS-NMR which can measure the ratio of one polymer to another. This quantity can be measured precisely without any other standards. The total polymer composition may be determined by carbon elemental analysis.

After the curative precursor is prepared, it is mixed together with the polymers of the blend. The required mixing and heating varies as a function of the polymers utilized, the curative precursor, and the operating conditions employed by the person of ordinary skill in the art, the essential factor being complete and excellent dispersing of the curative precursor. Therefore, depending upon the devices utilized (like Banbury™ mixers) to effect the mixing, the time may vary and may be determined by the person of ordinary skill in the art on the basis of his/her general knowledge and control of the properties of the composition used in the particular application, e.g., in the form of tire tread, knowing, e.g., that it is advisable to maximize the ratio of the 300% elongation modulus to the 100% elongation modulus for each composition. Thus, the thermomechanical work can include only a single step of suitable duration, temperature and intensity, or it can include several steps which can, if desired, be separated by at least a cooling step.

The final heating step of the method of the present invention is generally carried out using typical procedures known to one of ordinary skill in the art for crosslinking and curing polymer blends. In any event, the blend is heated sufficiently to obtain crosslinking, i.e., cure of the blend.

Although the invention has been illustrated by typical examples, it is not limited thereto. Changes and modifications of the examples of the invention herein chosen for purposes of disclosure can be made which do not constitute departure from the spirit and scope of the invention.

CLAIMS

1. A method for the preparation of a targetable solid for addition to a polymer blend of at least two polymers, said method comprising:

    treating the solid with at least a first polymer, and

    thereafter, optionally treating said treated solid with a second polymer having a greater affinity for the solid than said first polymer.

2. The method of claim 1 further comprising the step of heating the solid after contacting the solid with the first or second polymer.

3. The method of claim 1 wherein the solid is a filler and is selected from the group consisting of silica, bentonite, clay, titanium oxide, calcium carbonate, lignin, talc and resins.

4. The method of claim 3 wherein the filler is pretreated with a curative.

5. The method of claim 1 wherein the polymers are selected from the group consisting of thermoplastic and thermoset polymers, and mixtures thereof.

6. The method of claim 1 wherein the polymers are polybutadiene and a halogenated copolymer of isobutene and 4-methylstyrene.

7. A solid targetable filler produced according to the method of claim 1.

8. A solid targetable curative produced according to the method of claim 1 or 4.

9. A method for the preparation of a polymer blend comprising a solid, two or more polymers, wherein said solid is dispersed throughout at least one polymer blend component, said method comprising:

contacting said solid with a minor amount of at least a first polymer having affinity for said solid, and

thereafter, optionally contacting said contacted solid with a minor amount of a of a second polymer having a greater affinity for said solid than said first polymer, and

mixing the contacted solid with polymer(s) components to form a polymer blend.

10. The method of claim 9 further comprising the step of heating the solid after being contacted with the first or second polymer before mixing the solid with the polymer(s) components to form a polymer blend.

11. The method of claim 9 wherein the solid is selected from the group consisting of clay, silica, bentonite, talc, calcium carbonate, lignin, resins, and titanium oxide.

12. The method of claim 9 wherein the polymer blend components are selected from the group consisting of thermoplastic and thermoset polymers, and mixtures thereof.

13. The method of claim 9 wherein the polymer for contacting with the solid comprises polybutadiene and a brominated copolymer of isobutene and methylstyrene, and the solid comprises a filler.

14. The method of claim 13 wherein the filler is pretreated with a curative.

15. A blend produced according to claim 9.

16. A blend produced according to claim 10.

17. A polymer blend comprising:

a first polymer blend component and at least a second polymer blend component and a polymer treated solid, wherein the solid is treated with at least one polymer.

18. The polymer blend of claim 17 wherein the solid is treated with at least two polymers.

19. The blend of claim 17 wherein the polymer blend components comprise polybutadiene and a brominated copolymer of isobutene and methylstyrene.

20. The blend of claim 17 wherein the solid comprises a filler.

21. The blend of claim 17 or 20 wherein the solid is treated with at least one of the polymer blend components.

22. The blend of claim 17 or 20 wherein the solid is treated with two of the polymer blend components.

23. The blend of claim 20 wherein the filler is pretreated with a curative.

24. A method of curing a polymer blend of at least two polymers, said method comprising:

subjecting the blend of claims 20, 21, or 22 to curing conditions.

25. The method of claim 24 wherein the polymers of the blend comprise polybutadiene and a brominated copolymer of isobutene and methylstyrene.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/22504

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J3/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08J C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 480 057 A (SANO HIRONARI) 30 October 1984 see claim 1	1,17
X	US 5 135 971 A (STEIERT PETER ET AL) 4 August 1992 see claim 1	1,17
A	GB 1 090 972 A (DUNLOP RUBBER COMPANY LIMITED) 15 November 1967 see claim 1	1
A	DE 18 06 118 A (AMICON CORP.) 21 May 1970 see claims 1,3 see page 4, line 11 - line 15	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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